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Description

Adhesive sheet for implanting electrical modules in a card body

10 The invention relates to a blend of at least one thermoplastic and a synthetic rubber, this blend being activated with an implanting die at 150°C and being used for bonding electrical modules to card bodies.

15 In relation to the implanting of electrical modules in card bodies the prior art has already disclosed a multiplicity of adhesive sheets or joining methods. The aim of such implantations is to produce telephone cards, credit cards, parking machine cards, insurance cards, etc. Examples of the corresponding adhesive bonding methods are found for example in patents EP 0 842 995 A, EP 1 078 965 A, and DE 199 48 560 A.

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In this field of adhesive bonding, however, the bar is continuously being raised as regards the requirements imposed on the adhesive system. For instance, the adhesive must adhere well to polycarbonate, to ABS, PVC, and PET, and also to the electrical module. Bonding here is generally to epoxy materials, polyesters or polyimide. At one time cyano
25 acrylates were used as liquid adhesives, and have the advantage of optimum wetting of both the card body and the electrical chip. This technology, however, is dying out, since the operations are very slow. The evaporation of the solvent from the cavity in the card body was slow; the metering nozzles became blocked during downtime, as a result of drying out, and were also of poor meterability; and the liquid adhesive likewise required a
30 certain time for curing. As a result, the quality of adhesive bonding was decidedly poor.

It is here that the hot-melt adhesives prove markedly superior to their liquid counterparts. Nevertheless, here as well, the selection of suitable compounds is very limited, owing to the exacting requirements imposed on this joining technique. One restriction involves the
35 very different materials that must be bonded. Owing to the very different polarities of PC,

PVC, PET, ABS, epoxy, and polyimide, it is impossible to find a single polymer which adheres equally well to all materials. One possibility for raising the adhesion on various substrates is to mix different adhesives. Here again, however, the problem exists of obtaining a stable mixture, which is stable over a very long period of time even as a microphase-separated system, for example, and with no deterioration in adhesion. This is so in particular even for relatively long storages at elevated temperatures.

Moreover, the requirements imposed by the end customers are rising further and further. For example, the flatness of the electrical module with the card body is an important criterion, since otherwise it would no longer be possible to read the cards. This implies an upper limit on the implanting temperatures, since, for example, PVC in particular tends to deform at implanting temperatures above 170°C.

This is a particular problem for adhesives based on nitrile rubber, since even in conjunction with phenolic resins these adhesives require very high activation temperatures and exhibit only a low flow behavior.

Another criterion is the requirement from the banking sector that the electrical modules should not be able to be removed without destruction. Accordingly the internal cohesion of the adhesive must be very high, so that it does not split in the middle and the adhesion to either side (card body + electrical module) is extremely high. At the same time, however, the adhesive must also have a very high flexibility, since following implantation the cards pass through torsion tests and a flexural test. Preferably the card material ought to break before any failure of adhesion to the card body and to the electrical module. In general not even instances of lifting at the edge are tolerated.

A further criterion are temperature fluctuations and the effect of moisture, since in the course of their subsequent use these cards must withstand both high and low temperatures and in some cases are even required to survive a transit through the wash. Accordingly, the adhesive ought not to become brittle at low temperatures, ought not to liquefy at high temperatures, and ought to possess a low propensity to absorb water.

A further requirement criterion, owing to the growing numbers of card demand, is the processing speed. The adhesive ought to soften or melt very quickly, so that the implanting operation can be concluded within a second.

The object on which the invention is based, in view of this prior art, is that of specifying an adhesive sheet for implanting electrical modules in a card body, the said sheet meeting

the criteria specified above and developing very high adhesion to the different card bodies and electrical modules in the die in particular at implanting temperatures of 150°C.

In accordance with the invention the object is achieved by means of an adhesive sheet
5 composed of a blend of a synthetic rubber S1 and a thermoplastic T2, the blend

- a) being microphase-separated,
- b) possessing at least two softening temperatures, at least one softening temperature being greater than 65°C and less than 125°C,
- c) a storage modulus G' at 23°C, as measured by test method A, of greater than
10 10^7 Pas,
- d) a loss modulus G'' at 23°C, as measured by test method A, of greater than 10^6 Pas,
- e) and a crossover (same value of storage modulus and loss modulus), as measured by test method A, of less than 125°C.

15 Microphase separation for the purposes of the invention means that thermodynamically incompatible components segregate into spatially separate regions, but without macroscopic phase separation. The result, depending on composition, is phases of different structure.

20 Typical methods of ascertaining the presence of microphase separation include for example the following:

- transmission electron microscopy (TEM) for materials which exhibit different interaction with staining agents;
- atomic force microscopy (AFM) via the surface topology, a contrast in hardness or
25 adhesion;
- scattering methods (neutron scattering, small-angle X-ray scattering) in the case of materials with phases which exhibit a difference in material/radiation-action cross section;
- calorimetric methods, such as differential thermocalorimetry (DSC) or differential
30 thermoanalysis (DTA), and also rheological measurements for materials with phases differing in softening points;
- NMR spin diffusion for materials with phases differing in dynamics.

For the invention it is not necessary that the correspondingly observed or measured microphase separation produces "ideal" structures. In actual fact the microphase
35 separation observed on pressure-sensitive adhesives of the invention produces such

ideal structures only in the marginal case, but this is in no way contradictory to the inventive teaching.

Rather, by controlling the quality of the microphase separation, it is possible advantageously to exert an influence on the technical adhesive properties of the pressure-sensitive adhesives.

Furthermore, the crossover temperature must be below 125°C, since otherwise the adhesive will not become fluid and hence would not provide optimum wetting either of the card surface or of the electrical module. At the crossover point there is intersection of the storage modulus G' and loss modulus G'' curves; physically this can be interpreted as the transition from elastic to viscous behavior.

Furthermore, the elastic component, i.e., the storage modulus G', must be greater than 10⁷ Pas, and the viscous component, i.e., the loss modulus G'', must be greater than 10⁶ Pas, since otherwise the adhesive is not ensured optimum flexibility. The adhesive must ensure the loadings that occur between card body and electrical module even under instances of severe distortion. Hence the need for a rheologically optimized viscoelastic behavior.

The inventive mixture of the blend produces an improvement in the adhesion to the card body, which is achievable in an optimum way using a blend.

In a further preferred embodiment of the invention an adhesive sheet is used for implanting electrical modules with card bodies, the adhesive sheet being composed of a blend of a nitrile rubber and a thermoplastic T2, and

- a) the blend is microphase-separated
- b) the blend possesses at least two softening temperatures, at least one softening temperature being greater than 65°C and less than 125°C,
- c) it possesses a storage modulus G' at 23°C, as measured by test method A, of greater than 10⁷ Pas,
- d) it possesses a loss modulus G'' at 23°C, as measured by test method A, of greater than 10⁶ Pas,
- e) and it has a crossover, as measured by test method A, of less than 125°C.

In one further very preferred version of the invention use is made of microphase-separated blends of nitrile rubber and thermoplastic,

- a) the nitrile rubber possessing a softening temperature of -80°C to 0°C
- b) the thermoplastic possessing a softening temperature of 65°C to 125°C
- c) the nitrile rubber being insoluble in the thermoplastic.

5 By softening temperature is meant here a glass transition temperature for amorphous systems and a melting temperature in the case of semicrystalline polymers. The temperatures indicated here correspond to those obtained by quasi-steady-state experiments, such as DSC (differential scanning calometry), for example.

10 The weight fraction of the nitrile rubber in the thermoplastic is preferably between 2% and 60% by weight, with particular preference between 5% and 50%.

The adhesive bonding of the electrical module 2 to a card body 3 to produce what is shown as a chip card is depicted diagrammatically in Fig. 1. The inventive temperature-
 15 activable adhesive 1 possesses a layer thickness of between 10 and 100 µm in one preferred version and a layer thickness of 30 to 80 µm in a particularly preferred version.

The mixing with the synthetic rubber S1 achieves a reduction in viscosity under implanting conditions. The composition therefore does not flow out of the cavity in the
 20 card, even when the implanting temperature is increased, and hence makes a full contribution to adhesive bonding.

Synthetic rubbers S1

The inventive heat-activable adhesive is composed of a blend of at least one synthetic
 25 rubber S1 and at least one thermoplastic polymer T2.

In one very preferred version synthetic rubbers S1 used are polyvinyl butyral, polyvinyl formal, nitrile rubbers, nitrile-butadiene rubbers, hydrogenated nitrile-butadiene rubbers, polyacrylate rubbers, chloroprene rubbers, ethylene-propylene-diene rubbers, methyl-
 30 vinyl-silicone rubbers, fluorosilicone rubbers, tetrafluoroethylene-propylene copolymer rubbers, butyl rubbers, styrene-butadiene rubbers.

Nitrile-butadiene rubbers are available as Europrene™ from Eni Chem or as Krynac™ from Bayer, or as Breon™ and Nipol N™ from Zeon. Polyvinyl butyrals are available as Butvar™ from Solucia, as Pioloform™ from Wacker and as Mowital™ from Kuraray. Hydrogenated nitrile-butadiene rubbers are available as Therban™ from Bayer and as
 35 Zetpol™ from Zeon. Polyacrylate rubbers are available as Nipol AR™ from Zeon.

Chloroprene rubbers are available as Baypren™ from Bayer. Ethylene-propylene-diene rubbers are available as Keltan™ from DSM, as Vistalon™ from Exxon Mobile and as Buna EP™ from Bayer. Methyl-vinyl-silicone rubbers are available as Silastic™ from Dow Corning and as Silopren™ from GE Silicones. Fluorosilicone rubbers are available as Silastic™ from GE Silicones. Butyl rubbers are available as Esso Butyl™ from Exxon Mobile. Styrene-butadiene rubbers are available as Buna S™ from Bayer, and Europrene™ from Eni Chem, and as Polysar S™ from Bayer.

Polyvinyl formals are available as Formvar™ from Ladd Research.

In one preferred version the synthetic rubbers S1 possess a softening temperature of between -80°C and 0°C.

Thermoplastics T2:

The thermoplastic materials are selected preferably from the group of the following polymers: polyurethanes, polystyrene, acrylonitrile-butadiene-styrene terpolymers, polyesters, unplasticized polyvinyl chlorides, plasticized polyvinyl chlorides, polyoxymethylenes, polybutylene terephthalates, polycarbonates, fluorinated polymer, such as polytetrafluoroethylene, polyamides, ethylene-vinyl acetates, polyvinyl acetates, polyimides, polyethers, copolyamides, copolyesters, polyolefins, such as polyethylene, polypropylene, polybutene, polyisobutene, and poly(meth)acrylates, for example. The enumeration possesses no claim to completeness.

In one preferred version the thermoplastics possess a softening temperature of between 60°C and 125°C.

To optimize the technical adhesive properties and the activation range it is possible to optionally add bond strength-enhancing resins or reactive resins. The proportion of the resins is preferably between 2% and 50% by weight based on the blend.

Tackifying resins for addition that can be used include the tackifier resins that are already known and described in the literature. Representatives that may be mentioned include the pinene resins, indene resins, and rosins, their disproportionated, hydrogenated, polymerized, and esterified derivatives and salts, the aliphatic and aromatic hydrocarbon resins, terpene resins, and terpenephénolic resins, and also C5, C9, and other hydrocarbon resins. Any desired combinations of these and further resins may be used in order to adjust the properties of the resultant adhesive in accordance with requirements.

Generally speaking it is possible to use all resins that are compatible with (soluble in) the thermoplastic T2 and rubber S1; reference may be made in particular to all aliphatic, aromatic, and alkylaromatic hydrocarbon resins, hydrocarbon resins based on single monomers, hydrogenated hydrocarbon resins, functional hydrocarbon resins, and natural resins. Express attention is drawn to the depiction of the state of knowledge in the "Handbook of Pressure Sensitive Adhesive Technology" by Donatas Satas (van Nostrand, 1989).

In a further embodiment, reactive resins are added to the blend. One very preferred group embraces epoxy resins. The molecular weight M_w (weight average) of the epoxy resins varies from 100 g/mol up to a maximum of 10 000 g/mol for polymeric epoxy resins.

The epoxy resins embrace, for example, the reaction product of bisphenol A and epichlorohydrin, the reaction product of phenol and formaldehyde (novolak resins); and epichlorohydrin, glycidyl esters, the reaction product of epichlorohydrin and p-aminophenol.

Preferred commercial examples are Araldite™ 6010, CY-281™, ECN™ 1273, ECN™ 1280, MY 720, RD-2 from Ciba Geigy, DER™ 331, DER™ 732, DER™ 736, DEN™ 432, DEN™ 438, DEN™ 485 from Dow Chemical, Epon™ 812, 825, 826, 828, 830, 834, 836, 871, 872, 1001, 1004, 1031 etc. from Shell Chemical, and HPT™ 1071, HPT™ 1079 likewise from Shell Chemical.

Examples of commercial aliphatic epoxy resins are vinylcyclohexane dioxides, such as ERL-4206, ERL-4221, ERL 4201, ERL-4289 or ERL-0400 from Union Carbide Corp.

Examples of novolak resins which can be used include Epi-Rez™ 5132 from Celanese, ESCN-001 from Sumitomo Chemical, CY-281 from Ciba Geigy, DEN™ 431, DEN™ 438, Quatrex 5010 from Dow Chemical, RE 305S from Nippon Kayaku, Epiclon™ N673 from DaiNipon Ink Chemistry or Epicote™ 152 from Shell Chemical.

As reactive resins it is possible in addition to use melamine resins, such as Cymel™ 327 and 323 from Cytec.

As reactive resins it is also possible, furthermore, to use terpene-phenolic resins, such as NIREZ™ 2019 from Arizona Chemical.

5 As reactive resins it is also possible, furthermore, to use phenolic resins, such as YP 50 from Toto Kasei, PKHC from Union Carbide Corp., and BKR 2620 from Showa Union Gosei Corp.

10 As reactive resins it is also possible, furthermore, to use polyisocyanates, such as Coronate™ L from Nippon Polyurethan Ind. and Desmodur™ N3300 or Mondur™ 489 from Bayer.

In order to accelerate reaction between two components it is also possible, optionally, to additize crosslinkers and accelerants into the mixture.

15 Examples of suitable accelerants include imidazoles, available commercially as 2M7, 2E4MN, 2PZ-CN, 2PZ-CNS, P0505, L07N from Shikoku Chem. Corp. or Curezol 2MZ from Air Products.

20 In addition it is also possible to use amines, especially tertiary amines, for acceleration.

Besides reactive resins it is also possible to employ plasticizers. Here, in one preferred embodiment of the invention, plasticizers based on polyglycol ethers, polyethylene oxides, and phosphate esters can be used, as can aliphatic carboxylic esters and benzoic esters. In addition it is also possible to use aromatic carboxylic esters, diols of relatively
25 high molecular mass, sulfonamides, and adipic esters.

A further possibility is to add optionally fillers (e.g., fibers, carbon black, zinc oxide, titanium dioxide, chalk, solid or hollow glass spheres, microspheres made of other materials, silica, silicates), nucleators, expandants, compounding agents and/or aging
30 inhibitors, in the form for example of primary and secondary antioxidants or of light stabilizers.

In a further preferred embodiment polyolefins, especially poly- α -olefins, are added to the mixture. The company Degussa makes a number of different heat-activable poly- α -olefins
35 available commercially under the trade name Vestoplast™.

In one preferred embodiment the blends have static softening temperatures $T_{s,a}$ or melting points $T_{m,a}$ of 65°C to 125°C. The bond strength of these polymers can be raised by means of controlled additization. Thus it is possible, for example, to use polyimine copolymers or polyvinyl acetate copolymers as bond strength promoter additives.

The heat-activable adhesive serves in particular as an adhesive sheet for bonding electrical chip modules in card bodies, the respective adhesive layer developing very good adhesion to the card body and to the electrical chip module following temperature activation.

Production process

The inventive blends can be produced from solution or in the melt. For producing the blend in solution it is preferred to use solvents in which at least one of the components has good solubility. The mixture is produced using the known stirring equipment. For this purpose the introduction of heat may also be needed. Subsequently the blends are coated from solution or, more preferably, from the melt. For coating from the melt the solvent is removed from the blend beforehand. In one preferred embodiment the solvent is stripped off under reduced pressure in a concentrating extruder, something which can be accomplished using, for example, single-screw or twin-screw extruders, which preferably distill off the solvent in different or identical vacuum stages and possess a feed preheater. Coating then takes place via a melt die or an extrusion die, with the film of adhesive being drawn if desired in order to achieve the optimum coating thickness.

In one further embodiment of the invention the blend is produced in the melt. The resins can be mixed using a compounder or a twin-screw extruder, or a planetary roller extruder. Coating then takes place again from the melt. Coating takes place via a melt die or an extrusion die, with the film of adhesive being drawn if desired in order to achieve the optimum coating thickness.

Backing materials used for the blend are the customary materials familiar to the skilled worker, such as films (polyesters, PET, PE, PP, BOPP, PVC, polyimide), nonwovens, foams, woven fabrics, and woven films, and also release paper (glassine, HDPE, LDPE). The backing materials ought to have been provided with a release layer. In one very

preferred version of the invention the release layer is composed of a silicone release varnish or of a fluorinated release varnish.

5 Examples

Test methods:

Rheology A)

10 The measurement was carried out using a rheometer from Rheometrics Dynamic Systems (RDA II).

The Rheometrics Dynamical Analyser (RDA II) measures the torque which occurs when an oscillating shear is applied to a stripped sample (deformation control). The sample diameter was 8 mm, the sample thickness between 1 and 2 mm. Measurement was
15 carried out using the plate-on-plate configuration (parallel plates). The temperature sweep was recorded from 0 to 150°C with a frequency of 10 rad/s.

Iso-bending B)

The Iso-bending test is carried out in analogy to the Iso/IEC standard 10373:1993 (E) –
20 section 6.1. The test is passed if a total of more than 4000 bends is attained.

Extreme flexural test C)

In the extreme flexural test a cutout 3 cm wide, with the electrical module lying in the center, is cut from the chip card and then pressed together 10 x from a width of 3 cm to a
25 width of 2.5 cm. The test is passed if the electrical module does not become detached.

Hand test D)

In the hand test the chip card is bent by hand over one of the two corners lying closer to the electrical module, to an extent such that the card breaks or the module breaks. The
30 test in that case is passed. If the electrical module becomes detached or springs out, the test is failed.

Other test methods

The softening temperatures are determined preferably by way of differential scanning
35 calorimetry (DSC).

Molar masses were determined by GPC (gel permeation chromatography) measurements. (Preparation of a solution of the sample in tetrahydrofuran with a concentration of 3 g/l; dissolution at room temperature for 12 hours; subsequently, filtration of the solution through a 1 µm disposable filter, addition of approximately 200 ppm of toluene as internal standard.

Using an autosampler, 20 µl of the solution are chromatographed as follows: a 10³⊕ column 50 mm long is followed by one 10⁶⊕, one 10⁴⊕, and one 10³⊕ column, each with a length of 300 mm. The eluent used is tetrahydrofuran, which is pumped at a flow rate of 1.0 ml/min. The columns are calibrated with polystyrene standards, detection taking place by the measurement of the change in refractive index with the aid of a Shodex differential refractometer RI 71).

Investigations

Reference 1)
Polyamide film XAF 34.408 from Collano-Xiro

Reference 2)
PU film XAF 36.304 from Collano Xiro

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Example 1)

30% by weight of Breon N41 H80 (nitrile rubber) from Zeon and 70% by weight of Platamid 2395 (copolyamide) from Atofina were blended in a recording compounder from Haake at approximately 130°C for 15 minutes at 25 rpm. The heat-activable adhesive was subsequently extruded at 140°C between two plies of siliconized glassine release paper to 60 µm.

Example 2)

30% by weight of Breon N41 H80 (nitrile rubber) from Zeon and 70% by weight of Grilltex 1365 (copolyester) from EMS-Griltech were blended in a recording compounder from Haake at approximately 130°C for 15 minutes at 25 rpm. The heat-activable adhesive was subsequently extruded at 140°C between two plies of siliconized glassine release paper to 60 µm.

Example 3)

40% by weight of Breon N41 H80 (nitrile rubber) from Zeon and 60% by weight of Grilltex 1365 (copolyester) from EMS-Griltech were blended in a recording compounder from Haake at approximately 130°C for 15 minutes at 25 rpm. The heat-activable adhesive was subsequently extruded at 140°C between two plies of siliconized glassine release paper to 60 µm.

Implantation of electrical modules

The electrical modules were implanted in the card body using an implanter from Ruhlamat.

The materials employed were as follows:

Electrical modules: Nedcard Dummy N4C-25C, Tape-Type: 0232-10

PVC card: CCD

15 ABS card: ORGA

In a first step examples 1 to 3 are laminated at 2 bar onto the module belt from Nedcard, using a two-roll laminator from Storck GmbH.

The electrical modules are then implanted in the appropriate cavity in the card body.

20 The parameters employed were as follows for all the examples:

Heating step: 1

Die temperature: 150°C

Time: 1 x 2 s

25 Cooling step: 1 x 800 ms, 25°C

Pressure: 70 N per module

Results:

30 The chip cards produced using the inventive adhesives were tested by methods B, C, and D. The results are set out in Table 1.

Examples	Test method B	Test method C	Test method D
1	passed	passed	passed
2	passed	passed	passed

3	passed	passed	passed
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From table 1 it is apparent that all of the inventive examples met the principal criteria for a chip card and hence are very suitable for adhesively bonding electrical modules to card bodies.

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Tab. 2

Reference	Test method B	Test method C	Test method D
1	passed/failed on ABS	passed/failed on ABS	failed
2	failed	failed	failed

The reference specimens in table 2, in contrast, are significantly poorer and, especially on ABS card materials, do not pass the test methods.